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SPONSORED PROJECT INITIATION

Date: 3/2/81

Project Title: Polymer Mechanics in the Large-Deformation Region

Project No: E-19-646

Project Director: Dr. R. J. Samuels

Sponsor: National Science Foundation; Washington, D. C. 20550

Agreement Period: From 3/1/81 Until ~~8/31/82~~ ~~8/31/83~~ 9/30/84
~~(Includes usual 6 month unfunded flexibility~~ period)

Type Agreement: Grant No. DMR-8012692

Amount: $52,400 NSF
524 GIT (E-19-356)
$52,924 TOTAL

Reports Required: Annual Progress Report; Final Project Report

Sponsor Contact Person (s):

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Washington, D. C. 20550
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Defense Priority Rating: None

Assigned to: Chemical Engineering (School/~~Laboratory~~)

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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 1/28/85

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Includes Subproject No.(s) N/A

Project Director(s) Dr. R. J. Samuels GTRC / ~~GIT~~

Sponsor National Science Foundation, Washington, D. C. 20550

Title Polymer Mechanics in the Large-Deformation Region

Effective Completion Date: 9/30/84 (Performance) 12/31/84 (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [x] Final Invoice or Final Fiscal Report
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E-17-696

REQUEST FOR INCREMENT
FOR
A STRUCTURAL APPROACH TO SEMICRYSTALLINE POLYMER MECHANICS IN THE LARGE DEFORMATION REGION

GRANT NO. DMR-8012692

Submitted by

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to

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REVIEW OF PROGRESS TO DATE

Introduction

The objective of the present study is to develop the necessary knowledge of orientation effects (both crystalline and noncrystalline) in semicrystalline polymers to the point where the large deformation properties of these materials may be predicted from their structure. Initially the yield and failure of a series of uniaxially oriented isotactic polypropylene films, whose structural state is known, would be drawn at different rates and angles to the films axial direction. The data would then be examined for correlations between mechanical parameters such as the Hill yield criterion constants (1), the true stress at break, etc. and the crystalline, noncrystalline, and average molecular orientation functions of the films before deformation. Molecular state changes before, during, and after yielding would also be examined in order to elucidate the nature of these processes.

The purpose for choosing a uniaxially oriented system was that this should be the simplest system to analyze, and had the greatest chance for successful correlations. Once the significant structural criteria have been identified for this system, it would then be possible to attack the more complex multiaxial systems. Studies over the past year have indicated this was indeed a wise decision, especially if molecular processes during off-angle deformation in the high deformation region are to be explained and systematized.

Mechanical Studies

The first indication of the molecular significance of the off-angle deformation processes occurred late last year when the question of uniform states of stress arose. At that time we reported that horizontal lines placed on off-axis sample strips would rotate during deformation, and it was suggested this might be due to a non-uniform state of stress which could be corrected by the use of angular grips and sample aspect ratio charges. The problem has been studied this year, with measurements being taken both with angular and horizontal grips for samples cut at several (30^o, 45^o, and 60^o) off-axis angles. Within experimental error, no significant difference was observed in line rotation with sample deformation as a consequence of the grip design. This suggests the line rotation is a consequence of molecular realignment within the sample and not to grip or sample geometry problems.

A secondary problem which arose during this study was the prevalence of grip breaks. A grip break is premature failure at the edge where the grip holds the sample. Data obtained from such a break is discarded and hence a large amount of valuable sample and time is wasted. This problem has been largely eliminated by the use of a scaled-up version of a grip design developed for the Rheovibron (2) which allows alignment of the sample external to the tensile testing machine.

Structural Studies

The solution of a problem largely depends on the correct perception of the true nature of the problem; and that perception will depend on the techniques available for its elucidation. This was demonstrated earlier when the reason for the unusual mechanical behavior of the Series B films only became clear after the Trirefrigence technique (3) became available and showed the films were biaxial and not uniaxial as had been assumed.

(a) Trirefringence

The importance of the Trirefringence technique as a structural tool was apparent from such results, and further work was pursued to explore its limits and potential during the year. In particular, a series of isotactic polypropylene impact placques processed under different injection molding conditions became available. These samples offered the opportunity of using the Trirefringence technique on thicker moldings, and this in turn led to the need to develop techniques and computer programs which would analyze the data to determine the angle between the molecular symmetry axis and a reference direction, the principle refractive indices, the crystallinity and the axiality (see Figures 1 and 2). This work is continuing (4,5); however, the advances in both the Trirefringence technique and the characterization of molecular axiality achieved this year (6,7) now makes it possible to apply the technique to the study of molecular realignment (line rotation) during deformation of the off-axis uniaxial films.

Work has begun on determining the proper sample geometry to produce a drawn sample with the correct dimensions for analysis by this technique. Once this has been achieved, the axiality, crystallinity, and molecular symmetry axis shift with extension will be determined on the uniaxial films. These measurements are important since, much like a tenter film process, biaxiality may very well be occurring in these films during extension.

(b) Infrared Dichroism

Infrared Dichroism is a nondestructive technique for characterizing the molecular orientation in uniaxially oriented film samples. It can be used to determine orientation in biaxial films, but this requires a tedious and difficult sample tilting technique that has greatly limited its use for

FIGURE 1.

OPTICAL INDICATRIX PATTERNS FROM FAN GATED MOLDING OF ISOTACTIC POLYPROPYLENE

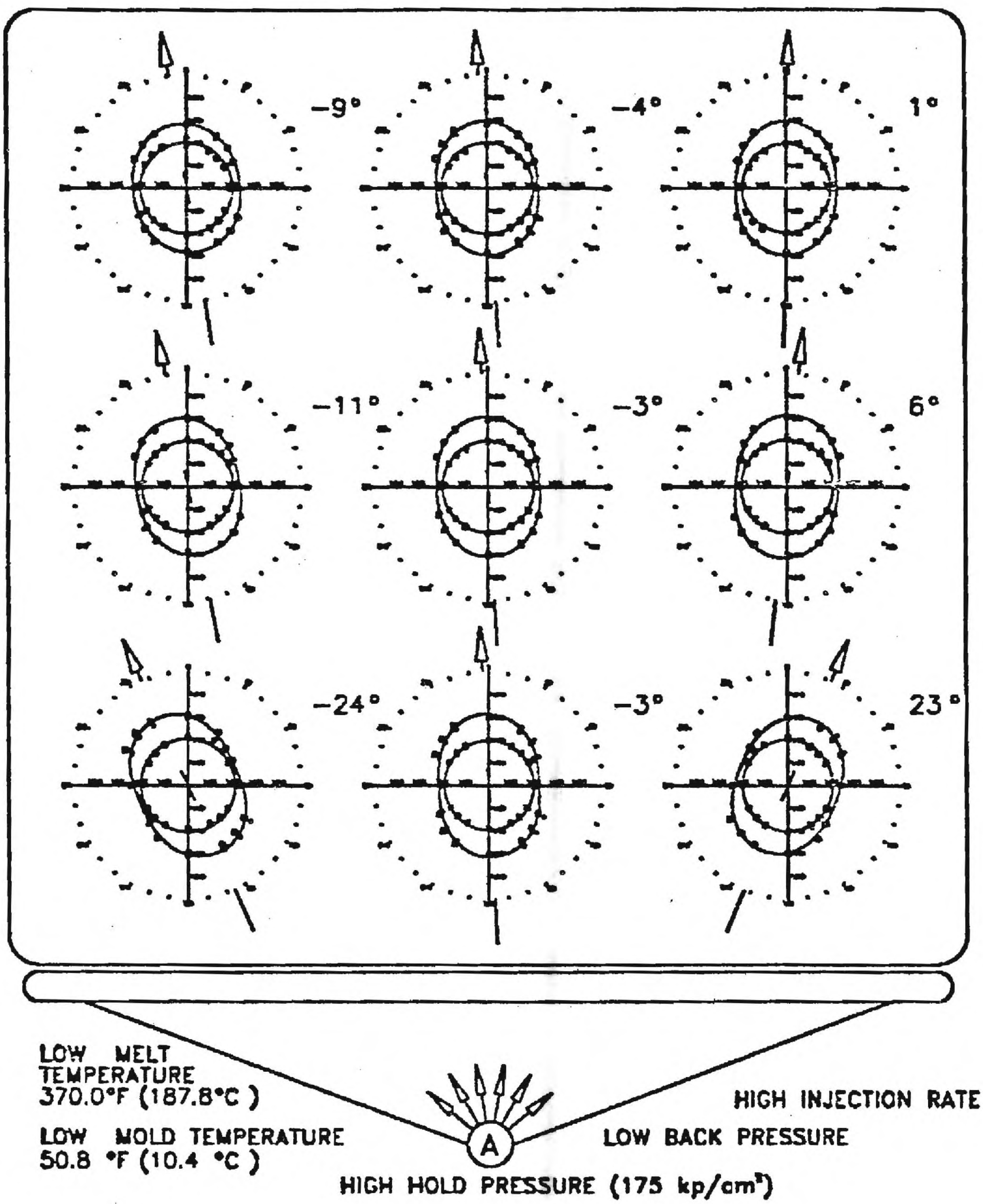
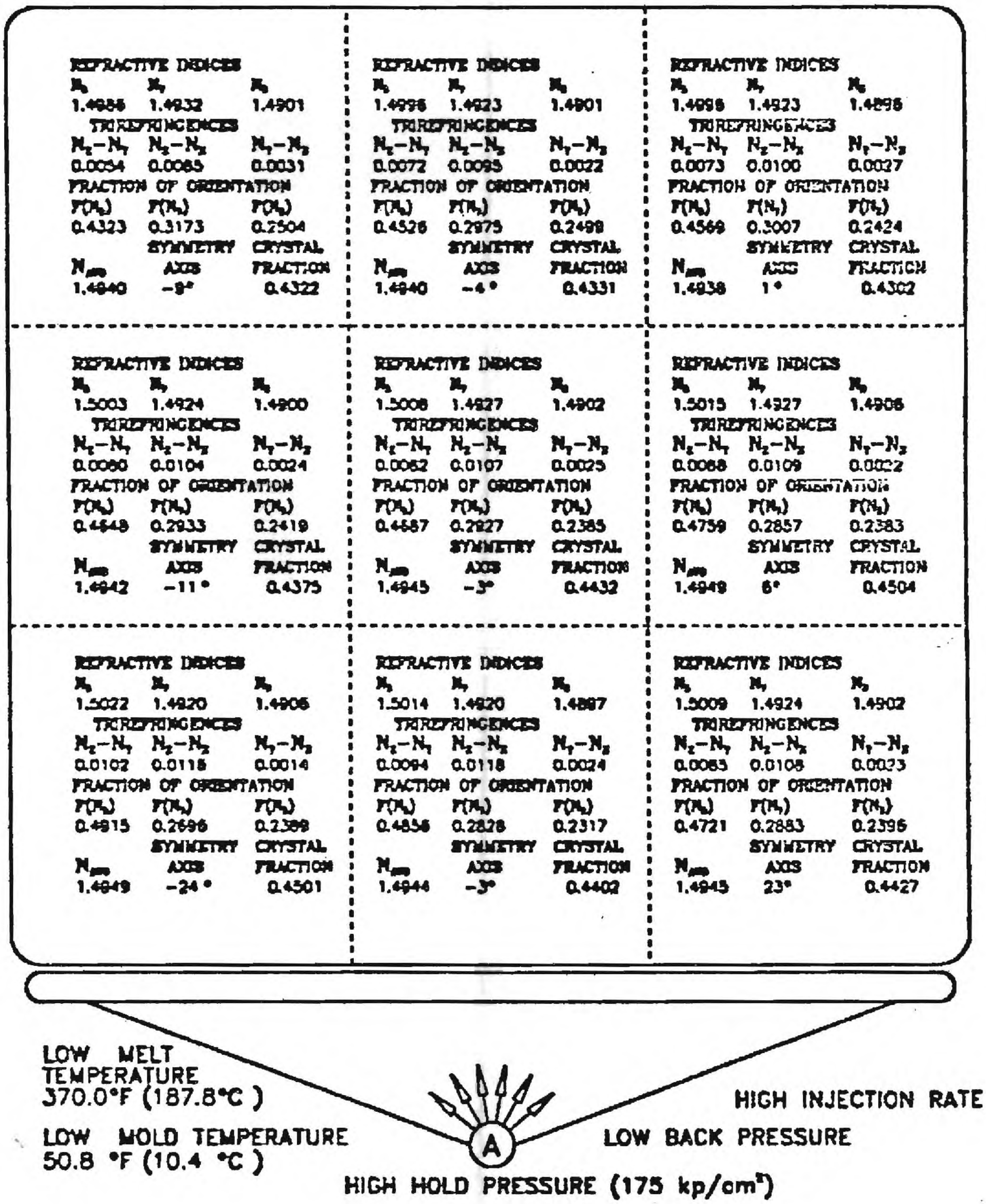


FIGURE 2.

OPTICAL CHARACTERISTICS OF FAN GATED MOLDING OF ISOTACTIC POLYPROPYLENE



this purpose. We have worked extensively on the biaxial problem this year and have overcome its limitation. Theoretical equations have been developed for quantitatively determining the three principle orientation functions (f_M - parallel to the molecular symmetry axis, f_T - perpendicular to the molecular symmetry axis in the plane of the film, and f_N - normal to the plane of the film) for the different phases (crystal and noncrystal) from infrared dichroism measurements, without the need for film tilting techniques. Instead of tilting the sample, all that is now needed is the dichroic ratio measured normal to the sample surface for two infrared bands whose transition moment angles are different and known quantitatively, and which absorb in the same phase (crystal or noncrystal). The operating equations have the form:

$$f_M = \left[\frac{3D_1(D_2-1)(D_{1,0}-1) - 3D_1(D_1-1)(D_{2,0}-1) + 3(D_1-1)(D_{2,0}-1)(D_1-D_2)}{2\ (D_{1,0}-1)(D_{2,0}-1)(D_1-D_2)}\right] - \frac{1}{2}$$

$$f_T = \left[\frac{3(D_2-1)(D_{1,0}-1) - 3(D_1-1)(D_{2,0}-1)}{2(D_{1,0}-1)(D_{2,0}-1)(D_1-D_2)}\right] - \frac{1}{2}$$

$$f_N = - f_M - f_T$$

where D_i is the measured transition moment of band i

$D_{i,o}$ is the intrinsic dichroic ratio calculated from the known transition moment angle, $\alpha_{\nu,i}$, of band i

$$D_{i,o} = 2 \cot^2 \alpha_{\nu,i}$$

and the f's have the definitions given above.

Experimental work to verify these equations was carried out this summer by an undergraduate student from the University of Washington (M. L. Samuels) hired under the grant. Because of the large number of measurements taken and the need to develop new techniques for angular measurements, rapid, less accurate scan rates were used. In spite of this limitation the correlation of data using five different crystal bands on six sample films was quite satisfactory (see Figure 3). All four points for each sample in the figure should be identical if the different crystal bands are yielding the same results. The close agreement for most of the samples seen in the figure, in spite of the fast experimental scan rates used, corroborates the equations. It also points out the need for very accurate determinations of the transition moment angles of these bands as well as more accurate measured dichroic data. This work will be presented at the March, 1983 ACS meeting in Seattle (8).

The significance of the infrared study goes far beyond the scope of the subject grant. True, it will now allow us to quantitatively characterize the molecular rearrangements occurring during deformation of the off-axis film samples, especially when the results are coupled with the optical Trire-fringence results on the same samples. However, these equations also mean that any uniaxial or multiaxial process can now be evaluated on a molecular level, conveniently, nondestructively, and quantitatively, provided the phase absorption and transition moment angle of the necessary bands have been characterized. Procedures for doing this have already been worked out by the principle investigator (9), not only for films but for thicker molded parts as well (10). Further, the recent developments in Fourier Transform Infrared (FTIR) means real-time characterization of the dynamics of these molecular

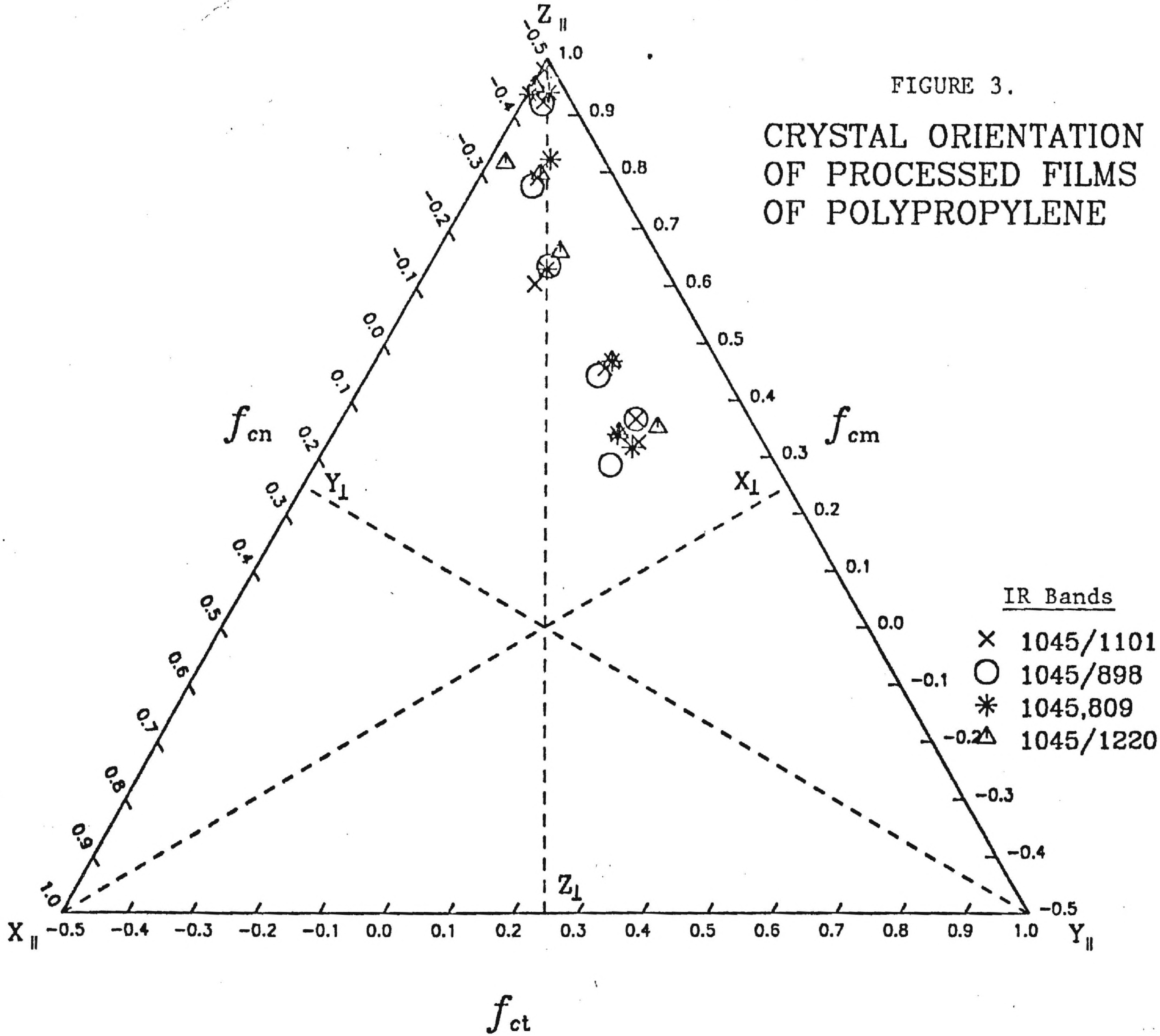


FIGURE 3.

CRYSTAL ORIENTATION OF PROCESSED FILMS OF POLYPROPYLENE processes can be carried out through the use of the above equations. Certainly, this work will be continued in the coming year with particular application to the acquisition of precise transition moment angles, phase identification of more infrared bands, and characterization of the molecular deformation processes occurring during off-axis deformation.

Analysis of Angular Data

For the plane-stress situation of a tensile test the Hill yield criterion (1) for a material of orthorhomic symmetry has the form:

$$\sigma^2\{A\cos^4\theta + B\sin^2\theta\cos^2\theta + C\sin^4\theta\} = 1$$

where σ is the yield stress, Θ is the angle between the tensile testing direction and the original draw direction of the film, and A, B, and C are parameters which characterize the anisotropy of the yield behavior. That is, for a given sample at a certain strain rate and temperature, A, B, and C are fitting constants that allow prediction of the yield behavior at angles other than those tested.

The thrust of the present study is to give molecular significance to these constants so that the yield behavior of a film may be predicted from its structural state parameters (the crystal fraction and the orientation functions). Preliminary results on two of the uniaxially oriented films support this approach. Figure 4 shows the experimental values and fitted Hill equation curves for two films. The birefringence of the most oriented film was 27×10^{-3} and of the less oriented film was 22×10^{-3}. The most significant aspect of these curves is their convergence at 45° and only small deviation beyond 15°. This suggests that for this set of uniaxial samples, B and C may remain constant with only A varying with orientation.

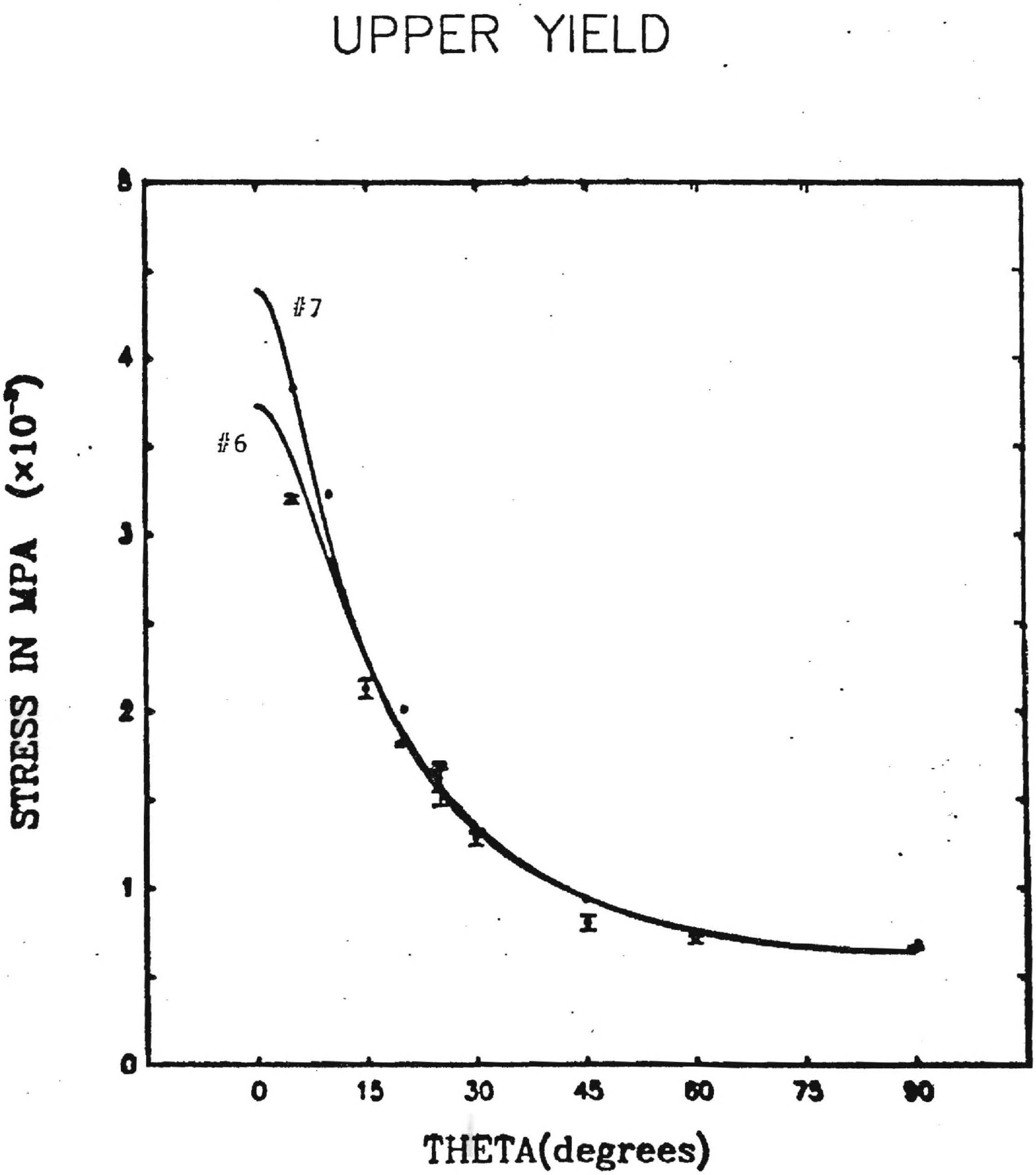


Figure 4. Relation between the yield stress and the angle theta between the testing direction and the sample processing direction for uniaxially oriented isotactic polypropylene films. Solid lines are calculated from Hill equation. Sample #7-- $\Delta_T = 27 \times 10^{-3}$, Sample #6--$\Delta_T = 22 \times 10^{-3}$.

Such a simple result would be consistent with reductions possible for compliance equations (11) and supports continuance of this approach.

The observed axial rotation during deformation does not imply that yield strength and true stress at break will not correlate with the initial structural state of the sample. Indeed, it is most probable that major rotation occurs at yield and uniaxiality is again achieved in the strain hardening region before failure. Thus the multiaxiality problem probably is significant only in the region between the onset of yielding and the beginning of strain hardening. If this is true then yield strength and true stress at break will likely correlate with initial structure. Certainly, earlier results (12,13,14) have shown this is indeed the case for drawing along the symmetry axis (0^{o}).

Thus the past year has been particularly rewarding. Not only have we acquired a deeper understanding of the nature of the molecular deformation mechanisms that must be considered if structural equations predicting polymer mechanics in the large deformation region are to be achieved, but new techniques and equations have been developed which can produce the necessary information. The stage is thus set on all-out assault on the problem.

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PLANS FOR NEXT YEAR

The identification during the past year of the molecular nature of the off-axis mechanical deformation problems, in conjunction with the development of new techniques and hence capabilities to attack these problems, leads us directly and logically into the sequence of work to be achieved during the next year.

1. Measurements will continue on the deformation of the uniaxial and subsequently the biaxial (B series) oriented films around angles at different rates of extension.

2. Models will be developed and tested to predict the rate and directional dependence of yield and failure. Special attention will be given to developing a molecular structure basis for the Hill yield criterion so that it may be used for predictive purposes.

3. Sample geometry studies will be completed so that the resulting deformed samples will be suitable for analysis by both the Trirefringence and infrared dichroism techniques.

4. Line rotation and molecular orientation processes will then be examined during deformation of these newly designed uniaxial and biaxially oriented samples using the new characterization techniques.

The amount of work required to achieve these goals is formidable. For just one film at a single rate of deformation at just one angle, samples will be needed before yielding, just after yielding at subsequent stages during the deformation and into the strain hardening region. That one film however, will be examined not at one angle but at angles of 0^0, 30^0, 45^0, 60^o, and 90^o and for assurance, more than one run of some of these samples should be made. To physically prepare the samples, run them and subsequently study them by Trirefrigence and infrared dichroism is too much for one student. I am therefore requesting the support of two graduate students; one to do the mechanics and optics and the other to concentrate on the development of the infrared dichroism technique and the study of the off-axis deformation mechanisms.

STATEMENT OF RESIDUAL FUNDS

It is expected that less than 10% of the present budget will remain as of the requested increment date.

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT

NSF FORM 98A

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PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology Atlanta, Georgia 30332	Polymers	DMR-8012692
	4. Award Period From 3/1/81 To 9/30/84	5. Cumulative Award Amount 171,100

6. Project Title
A Structural Approach to Semicrystalline Polymer Mechanics in the Large Deformation Region

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

The purpose of this study was (a) to examine the effect of semicrystalline polymer structure on the observed yield and failure (both along, and at angles to, the molecular symmetry axis) in order to determine if the critical macroscopic mechanical behavior in the high deformation region (yield and failure) was determined by (or coupled to) the initial structure before deformation; and (b) to develope analytical functions relating the macromechanics to the structure if such coupling was observed. Isotoctic polypropylene was used as the model system and both stress-strain and structural measurements were made. The structural information requirements of the study resulted in the development of new polarized refractometer and infrared techniques and analyses, while new grips were designed for the stress-strain measurements and macromechanic equations were derived for the specific conditions of the test. The yield and failure of the samples, ranging from low to high initial orientation, were measured at different rates and found to vary with their initial structural state. Analytical functions were then developed that predicted the yield and failure stress both axially and around angles to the symmetry axis of the samples directly from orientation functions of the samples before stretching. Further, two equations were found which predicted the yield strain of the samples from the same structural orientation functions. The results suggested that noncrystalline orientation controls the deformation but were not conclusive on this point.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

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